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# General Rule for Displacive Phase Transitions in Perovskite Compounds Revisited by First Principles Calculations

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A recent high pressure experiment on  $\text{LaAlO}_3$  has revealed that the compound is an exception for the “general rule” of displacive phase transition associated with zone-boundary phonons. In the present study, the experimental result is successfully confirmed by first principles calculations. The pressure dependence of phonon frequencies as well as the phase transition pressure is quantitatively well reproduced. We found that the behavior is not peculiar to  $\text{LaAlO}_3$  but rather ubiquitous.  $\text{RAiO}_3$  ( $R = \text{La}, \text{Nd}, \text{Sm}, \text{and Gd}$ ) and  $\text{LaGaO}_3$  can be classified in the same group.

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Compounds having perovskite-type structure as denoted by  $\text{ABX}_3$  have been popular targets of fundamental investigations since they exhibit a wide variety of physical properties depending upon chemical composition, defects, and small changes in atomic arrangements. Many of these compounds do not show ideal cubic perovskite structure under ordinary conditions. They often undergo a series of phase transitions. The transition sometimes induces ferroelectricity, which plays important roles in modern technology and fundamental science.  $\text{BaTiO}_3$  is a typical example in this category. Other compounds such as  $\text{LaAlO}_3$  do not exhibit ferroelectricity. Their atomic displacement associated with the transition can be described simply by the rotation of the  $\text{BX}_6$  octahedron. Since the atomic displacement corresponds to a phonon mode at the Brillouin zone boundary of the cubic phase, this type of transition has been called zone boundary transition (ZBT).

$\text{LaAlO}_3$  is a good model compound that undergoes ZBT exclusively, which has been extensively studied. It is known to show cubic to rhombohedral ZBT at around 800 K on cooling under ordinary pressure [1,2]. The transition has been characterized by softening and condensation of the Brillouin zone boundary  $R_{25}$  mode [3–5]. The condensation of the  $R_{25}$  mode brings oxygen atom displacement which manifests itself as a rotation of a virtually rigid  $\text{AlO}_6$  octahedron. The temperature variation of the degree of octahedron rotation has been investigated by a number of techniques. However, in the early days it was not possible to determine the tiny octahedral rotation in the vicinity of the phase transition without using a special technique such as electron spin resonance on  $\text{Fe}^{3+}$  doped samples [1]. Precise neutron diffraction study to determine the rotational angle was reported only very recently [6]. It was also recently that the pressure induced rhombohedral to cubic transition of  $\text{LaAlO}_3$  was reported by Bouvier and Kreisel [7] for the first time. They concluded that the rhombohedral to cubic transition occurs at around 14 GPa on the basis of the observation of soft mode frequency of Raman spectroscopy and x-ray superlattice reflection using synchrotron radiation. Their finding im-

plies that the transition temperature  $T_c$  decreases with the increase of pressure  $p$ , i.e.,  $dT_c/dp < 0$ . This is contrary to the long-standing empirical “general rule” of ZBT by Samara *et al.* [8] who claimed that a large number of compounds show  $dT_c/dp > 0$  without an exception. The dependence is opposite to that for ferroelectric phase transition associated with softening with zone-center phonons, i.e.,  $dT_c/dp < 0$ . If the behavior in  $\text{LaAlO}_3$  can be really verified, the general rule of ZBT should be reinvestigated.

First principles techniques have opened a gate toward quantitative analysis of many phenomena that are difficult to assess by experiments. Recent advances in computational technique enable us to determine full phonon dispersion [9–11]. Thereby the major contribution for finite temperature properties of crystals can be determined from first principles. In the present study, we use such a technique to examine the phase transition of  $\text{LaAlO}_3$ . We have adopted a projector augmented wave method [12,13] based on density functional theory in order to compute structure and dynamics of  $\text{LaAlO}_3$ . The exchange and correlation effects were treated by the generalized gradient approximation [14]. The  $k$  mesh was sampled according to a Monkhorst-Pack scheme with a spacing of  $0.4/\text{\AA}$ . The cutoff in the plane wave expansion was 500 eV. Convergence of relative energies with respect to the  $k$  mesh and energy cutoff was found to be better than 1 meV/atom.

Figure 1 shows total energy ( $E_t$ ) and pressure ( $p$ ) of the cubic and rhombohedral structures as a function of cell volume ( $V$ ). As for rhombohedral cells, we have performed geometry optimizations in which lattice constants and internal parameters were relaxed at constant volumes. Pressure was analytically obtained from the  $E_t$ - $V$  curve after fitting the  $E$ - $V$  curve to the third order Birch-Murnaghan equation. The use of two other equations, i.e., a Murnaghan equation and a polynomial equation, produced quantitatively the same results. Upon decreasing the volume, total energies of the two structures converge. The point of merge is approximately  $V = 51 \text{ \AA}^3$ , which corresponds to  $p = 13 \text{ GPa}$ . With approaching to the tran-

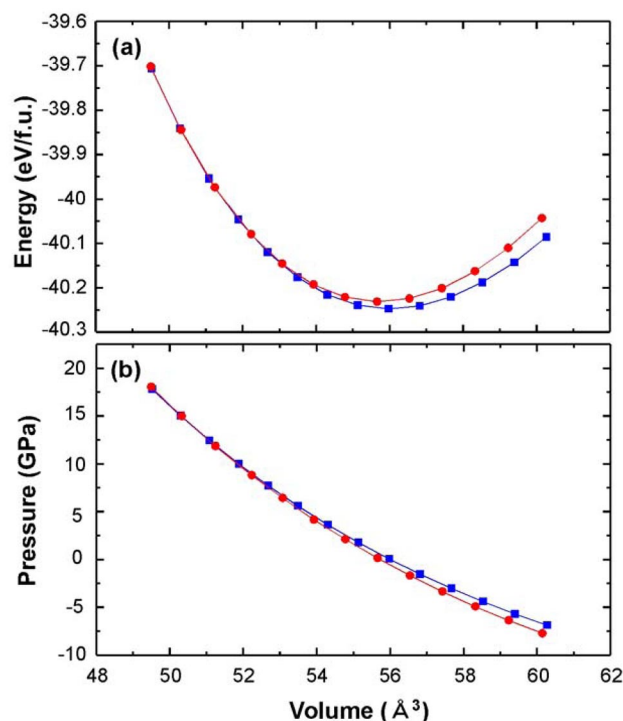


FIG. 1 (color online). (a) Total energy ( $E_t$ ) of two structures as a function of cell volume ( $V$ ). Circles and squares denote the energies for the cubic and the rhombohedral structures, respectively. (b) Pressure ( $p$ )-volume ( $V$ ) relations for the two structures.

sition, many structural parameters converge to the values in the cubic structure. For example, the ratio of cell constants, i.e.,  $c/a$ , converged to unity. Oxygen positional parameter  $x(\text{O})$  converged to  $1/2$ , and the rotational angle of  $\text{AlO}_6$  octahedron  $\phi$ , as calculated by  $\tan\phi = 2u\sqrt{3}$  with  $u = x(\text{O}) - 1/2$ , converged to zero. Adopting the Landau theory, the rotational angle  $\phi$  has often been used to represent the order parameter [1], and  $\phi^2$  should decrease linearly with temperature or pressure for a continuous second order phase transition. Also, the octahedral strain parameter  $\eta$ , as defined by  $\eta = (c/\sqrt{6}a)\cos\phi$ , has been used to discuss structures of compounds in this class [6,15]. Figure 2 shows the present computational results for the dependence of  $\phi^2$  and  $1 - \eta$  on  $p$  along with the experimental value that has been reported only at 0 GPa. The definition of  $\phi$  is shown in the inset of Fig. 2. The linearity can be clearly seen in these two plots. However, a small but clear deviation can still be found in the vicinity of the transition. This may be the limitation of the simplified Landau formalism. Extrapolation of the plots found that the transition pressure is approximately 13 GPa, which agrees well with that obtained from Fig. 1.

Because of a tiny difference in total energy associated with the rhombohedral distortion in the vicinity of the transition, the critical phenomenon is difficult to discuss only by means of static calculations. We have therefore adopted a dynamic method within the harmonic approxi-

mation. Lattice dynamics has been computed by the direct method [11]. Hellmann-Feynman forces by atomic displacements of  $0.03 \text{ \AA}$  for every symmetry nonequivalent atom were calculated using supercells obtained by expanding the primitive cells by  $2 \times 2 \times 2$  times. They were composed of 40 atoms for the cubic and 80 atoms for the rhombohedral structures. The force constant matrix and then the dynamical matrix were constructed. Phonon frequencies were obtained by the diagonalization of the dynamical matrix.

As can be found in Fig. 1, total energies of the two structures converge upon decreasing the volume. When the cell volume of the cubic structure is larger than the transition, it is expected to undergo a phase transition to the rhombohedral structure. Then, softening of a phonon mode is expected to take place at the Brillouin zone boundary  $R$  point. In other words, the softening should disappear when  $V$  is smaller than the transition. We made a series of phonon calculations to examine the dependence of the phonon frequency at the  $R$  point on the cell volume. The results are shown in Fig. 3. The negative value of squared frequency shows the imaginary harmonic frequency, which implies that the structure is unstable against the atomic displacements of the corresponding mode eigenvector. On

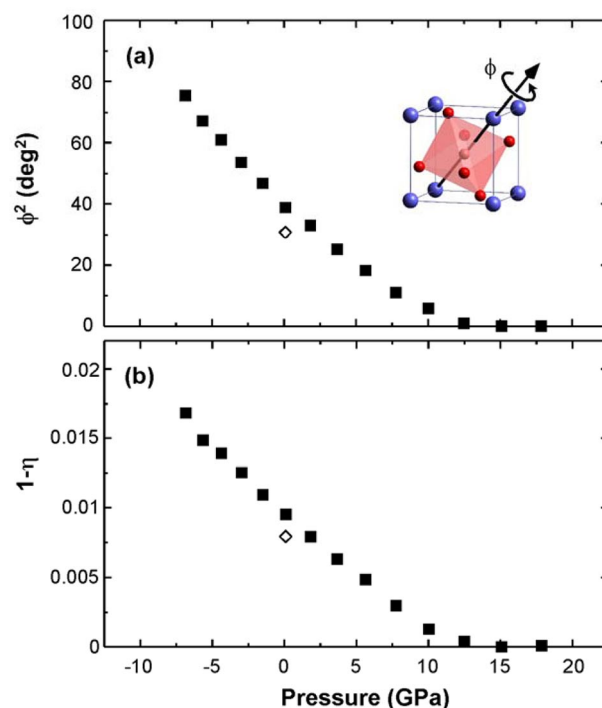


FIG. 2 (color online). (a) Pressure dependence of the square of the rotational angle  $\phi^2$ . The present computational results are denoted by the solid squares.  $\phi$  stands for the degree of octahedron rotation around  $[111]$  axis as shown in the inset. (b) Dependence of  $1 - \eta$  on  $p$ . The solid squares denote computational results.  $\eta$  measures the compression of octahedron in the direction parallel to the rotational axis. The experimental values at ordinary pressure are indicated by the open diamonds [6].

increasing pressure, the imaginary part of the harmonic frequency reduces and then disappears above the critical pressure where the cubic structure becomes stable. The critical pressure is 13 GPa, which is in good agreement with the pressure where the order parameter  $\phi^2$  reaches zero, as shown in Fig. 2.

Another set of phonon calculations has been made for the rhombohedral structure. The pressure dependence of frequencies of three Raman active modes in the rhombohedral structure is shown in the second panel of Fig. 3. Experiments by Bouvier and Kreisel [7] have focused on the pressure dependence of the  $A_{1g}$  mode at 124  $\text{cm}^{-1}$  and two  $E_g$  modes at 154 and 488  $\text{cm}^{-1}$ . The  $A_{1g}$  mode is known to correspond to the  $R$  phonon mode in the cubic phase. Significant softening of the  $A_{1g}$  mode with the increase of the pressure has been observed by the experiment. It eventually disappeared at the pressure of 14 GPa in

their experiments. The present calculations reproduce the experimental results satisfactorily. The square of the frequency for the  $A_{1g}$  mode  $\omega^2(A_{1g})$  decreases linearly. On the other hand, frequencies of two  $E_g$  modes increase almost linearly with the pressure. Theoretical  $\omega^2(A_{1g})$  became zero at 13 GPa, which agrees well not only with the experiments but also with the transition pressure of the cubic structure where the soft mode disappears.

Figure 3 shows that the instability of the cubic phase decreases with the increase of  $p$ . This implies that the transition temperature  $T_c$  to the cubic phase decreases with  $p$ , i.e.,  $dT_c/dp < 0$ . This is contrary to the empirical general rule of ZBT by Samara *et al.* [8]. They claimed that there were no exceptions to the rule  $dT_c/dp > 0$  for ZBT and  $dT_c/dp < 0$  for transitions associated with soft zone-center optic phonons.  $\text{LaAlO}_3$  should be an exception for the rule.

Now the following question arises: Is the present case the only exception to the rule, or rather ubiquitous among many compounds? In order to answer this question, we have performed a series of calculations for perovskite oxides. Systems investigated here are  $\text{RAIO}_3$  compounds with  $R = \text{Nd, Sm, Gd, Dy, and Er}$ . They allow us to examine the effect of the  $A$  site cation size. In order to examine the size of the  $B$  site cation, we made calculations for  $\text{LaGaO}_3$  and  $\text{NdGaO}_3$  as well.  $\text{NdAlO}_3$  and  $\text{SmAlO}_3$  are analogous to  $\text{LaAlO}_3$ , which are known to exhibit rhombohedral to cubic phase transition under ambient pressure. Crystal structures and phase transition temperatures under ambient pressure [16–18] are summarized in Fig. 4 together with ionic radii [19] of constituents. The tolerance factor  $t$  is often used to discuss the effect of ionic size on properties of perovskite compounds. It is defined as  $t = (r_A + r_O)/\sqrt{2}/(r_B + r_O)$ , where  $r_A$ ,  $r_B$ ,  $r_O$  are the ionic radii of the  $A$  site cation, the  $B$  site cation, and the oxygen ion, respectively.

Figure 5 shows the frequency of the zone boundary  $R$  point mode versus the normalized volume calculated for

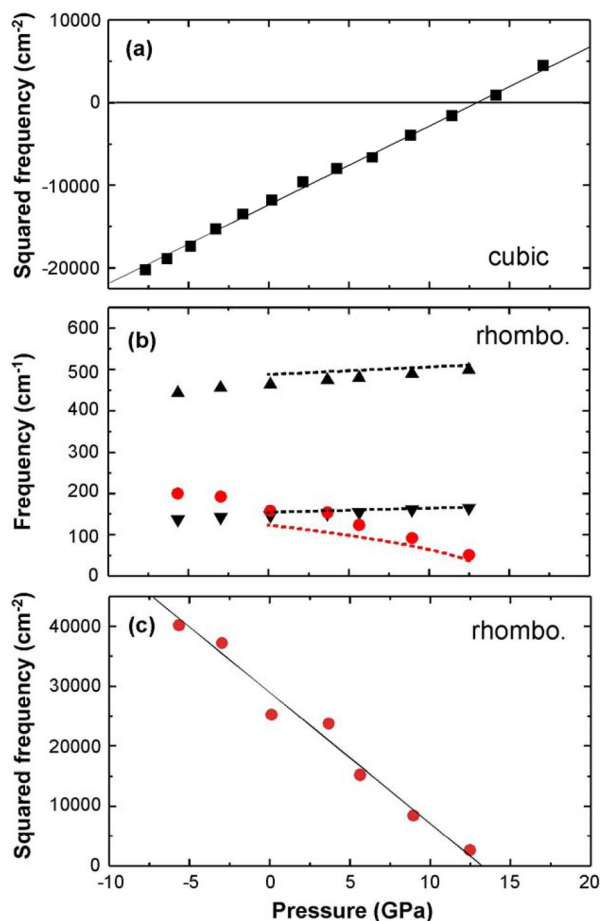


FIG. 3 (color online). (a) Pressure dependence of the squared frequency of the phonon mode at the Brillouin zone boundary  $R$  point for the cubic cells. (b) Pressure dependence of the frequencies for Raman active modes for the rhombohedral structure. Calculated frequencies of the  $A_{1g}$  mode and two  $E_g$  modes are denoted by the circles and triangles, respectively. Experimental data are denoted by dashed lines [7]. (c) The squared frequency of the soft  $A_{1g}$  mode for the rhombohedral structure as a function of pressure.

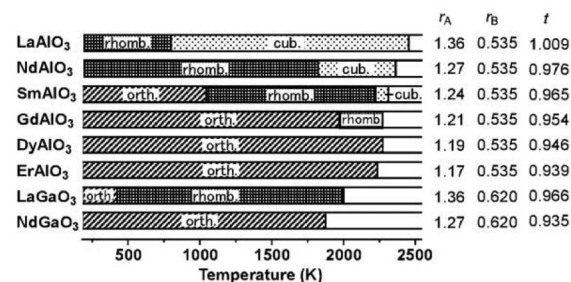


FIG. 4. Evolution of stable phases with temperature under ambient pressure for compounds of interest. Phase transition temperatures are taken from Refs. [16–18]. Zones not hatched indicate the liquid phases. Also shown are ionic radii of  $A$  site and  $B$  site cations,  $r_A$  and  $r_B$ , and the tolerance factor  $t$ , defined as  $t = (r_A + r_O)/\sqrt{2}/(r_B + r_O)$ . The ionic radii adopted here are 12-, 6-, and 6-coordinated values for  $A$  site and  $B$  site cations and the oxygen ion, respectively [19,20].



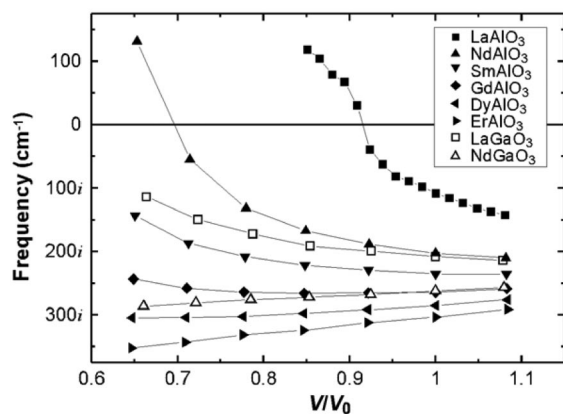


FIG. 5. Frequencies of zone boundary  $R$  point mode versus normalized volume for various compounds. Computed equilibrium volume of cubic structure was taken as  $V_0$ .

the cubic phases of eight compounds. Although no experimental data are available for the effect of pressure on the phase stability of these compounds except for  $\text{LaAlO}_3$ , five among eight of the compounds show the tendency that decreasing volume (increase in pressure) stabilizes the  $R$  point soft mode.  $\text{NdAlO}_3$  is expected to undergo a rhombohedral to cubic transition at the volume that corresponds to the pressure of approximately 80 GPa. Transition pressure should be even higher or transition is not induced by the pressure for the other compounds. Although such high pressure experiments are difficult, we can predict a negative value of  $dT_c/dp$  at lower pressures in these compounds. The five compounds can be classified in the same group as that of  $\text{LaAlO}_3$ , which is against the general rule for ZBT.

It is interesting to note that the dependence of the frequency of the zone boundary  $R$  point mode on relative volume tends to increase from a negative value to a positive value with the decrease of  $r_A$  in a series of  $\text{RAlO}_3$ . The dependence can be generalized among  $\text{RAlO}_3$  and  $\text{RGaO}_3$  if we take the tolerance factor as a variable parameter. A good correlation can be seen between the tolerance factor and the instability of the cubic phase among  $\text{RAlO}_3$  and  $\text{RGaO}_3$ . The relationship can be interpreted as follows: A tolerance factor larger than unity means that the  $A$  site cation is oversized relative to the  $B$  site cation. In such a situation, the cubic structures should be obtained as a compromise between the stretched  $B$ -O bond and the compressed  $A$ -O bond. The  $B$ -O bond is therefore easier to compress under pressure, which suggests the tendency to adopt ideal cubic structure under compression. On the other hand, with a smaller tolerance factor, the cubic structure comprises the stretched  $A$ -O bond and the compressed  $B$ -O bond, being  $B$ -O<sub>6</sub> octahedron more rigid and preventing the octahedron from compression. This could drive the system toward a more distorted structure (with a larger rotational angle of octahedron) in the presence of external pressure.

In conclusion, we found that the instability of the cubic perovskite structure decreased with pressure in a series of  $\text{RAlO}_3$  ( $R = \text{La, Nd, Sm, and Gd}$ ) and  $\text{LaGaO}_3$  through first principles calculations of phonon states. This is contrary to the empirical general rule of displacive phase transition associated with zone-boundary phonon. A good correlation between the tolerance factor and the instability is found among aluminates and gallates. A further systematic study should provide a deeper understanding of the problem and a more general rule for ZBT.

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